(12) EUROPEAN PATENT APPLICATION

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(54) **Near-azeotropic ternary compositions constituted by hydrogenated fluorocarbons as hydrocarbons, suitable as refrigerating fluids**

(57) Near-azeotropic ternary compositions of hydrofluorocarbons with n-butane or isobutane selected from:

A)	1,1,1,2-tetrafluoroethane (R134a)	65-94% by weight
	pentafluoroethane (R125)	2-25% by weight
	n-butane (R600) and/or isobutane (R-600a)	1-10% by weight
B)	1,1,1,2-tetrafluoroethane (R134a)	65-94% by weight
	1,1,1,2,3,3,3-heptafluoropropane (R227ea)	5-25% by weight
	n-butane (R600) and/or isobutane (R-600a)	1-10% by weight

Said compositions have zero ODP, very low GWP and good solvent power for mineral lubricants. They are utilizable as drop-in substituents of R-12 in domestic refrigeration.

EP 0 779 352 A1

Description

The present invention relates to near-azeotropic compositions utilizable as refrigerating fluids in circuits working according to the Rankine cycle. More particularly the present invention relates to compositions having zero ODP (Ozone depleting Potential) value and low GWP (Global Warming Potential) and VOC (Volatile Organic Compound) values, utilizable as low environmental impact substituents of dichlorodifluoromethane (R-12).

R-12 has been widely used as refrigerating fluid for circuits working at middle-high evaporation temperatures, typical of the domestic refrigeration and of the housing and motorvehicles air-conditioning. At present the manufacturing and marketing of R-12, and generally of chlorofluorocarbons, are submitted to restrictive rules in all the world for applications of this kind because of the alleged destroying power of this product on the ozone layer present in the stratosphere.

Therefore, the need of finding other products or compositions capable of effectively replacing R-12 without causing environmental damages, is particularly felt. For this purpose, it was suggested the use of hydrofluorocarbons (HFC) or hydrochlorofluorocarbons (HCFC), whose depleting potential with respect to ozone (ODP) is very low or even zero, as very low is also their contribution to the so called "greenhouse effect", measured by the GWP.

Among the various substitute products of R-12 up to now proposed, the most known is 1,1,1,2-tetrafluoroethane (R-134a), a product having a low environmental impact (ODP=0); GWP=0.35) and properties similar to those of R-12. However R-134a shows as refrigerant a coefficient of performance lower than that of R-12 and, on the other side, it is not compatible with the conventional lubricants of mineral type, therefore its use as refrigerating fluid requires on the one hand a new planning of the refrigerating circuit to avoid higher energy consumptions and on the other hand the substitution of the lubricating oil with another compatible oil. The oil conventionally used with R-12 is indeed of the mineral type while that required by R-134a belongs to the esterified polyols class and the two lubricants are not compatible.

In order to overcome the drawbacks shown by R-134a, alike other single refrigerants, the use of mixtures containing HFC has been proposed. However, if mixtures are used, other inconveniences are encountered. First of all, because of the different volatility of the components, fractionation occurs when passing from liquid phase to vapour phase and viceversa, with a remarkable variation in the condensation and evaporation temperatures, so as to impair even considerably the efficiency of the refrigerating circuit. Moreover, the filling up of the refrigerant, necessary in consequence of unavoidable losses from the refrigerating plant, cannot be carried out with the original mixture, but it is necessary to proportion the various components according to the exact composition of the mixture remained after fractionation, so as to restore the initial optimum composition. Lastly, if the mixture contains a more volatile, inflammable component, the vapour phase enriches in such component until the inflammability point is reached, with evident hazard during its use. Similarly, if the inflammable component is less volatile, it concentrates in the liquid phase, giving rise to an inflammable liquid.

In order to avoid such drawbacks, it is therefore convenient to use mixtures having an azeotropic behaviour, i.e. mixtures characterized in, that they behave as pure fluids. However, the obtainment of azeotropic mixtures is an extremely rare event, since it requires a particular combination of boiling temperatures and deviations from the ideal behaviour of the various components. Therefore, the study of refrigerating mixtures has been directed to the obtainment of "near-azeotropic" mixtures. The definition, among those suggested until now, which better suits the purposes of the present invention, is that according to which a near-azeotropic behaviour occurs if the percentage pressure variation in consequence of a 50% evaporation of the liquid (indicated as $\Delta p/p$ per 100) at 25°C is lower than 15% (in this respect see the article by **D.A. Didion and D.B. Bivens in Int. J. Refrig., vol. 13, p. 163 and following, 1990**).

A further characteristic desirable for the substituents of chlorofluorocarbons (CFC)-based refrigerants, as already mentioned, is that they shall not virtually require any modifications of elements, materials and, generally, components of the system in which they operate: in this case we can speak of "drop-in" substituents. In particular, it would be advantageous having a product or a mixture soluble in the lubricating mineral oils commonly used with conventional refrigerants, or soluble in an oil compatible with the oils used at present. In such a way, before introducing the new refrigerant, complex operations of complete discharging, accurate washing and drying of the refrigerating plants would be avoided.

In **EP 299614** various near-azeotropic mixtures of halocarbons are proposed as substituents of R-12 in the refrigerating field. The mixtures of this kind on the one hand still show not zero ODP values because of the presence of chlorine atoms in one or more components, on the other hand, according to what ascertained by the Applicant, require the use of an alkylbenzenic lubricating oil, with the drawbacks described above.

In **EP 565265** are described mixtures containing R-134a, an hydrocarbon selected from propane, propylene or isobutane and optionally octafluoropropane (R-218). Although these mixtures are an improvement compared with R134a used alone, they show the drawback of a notable deviation from the azeotropic behaviour. See in particular col. 3, lines 13-15.

In **EP 638623**, in the name of the Applicant, mixtures as substituents of R-12 and R-502 are described, however some of them have not the feature of being "drop-in", while for others it has been found that they do not have sufficient chemical stability during the use.

The Applicant has unexpectedly found that HFC-based mixtures containing hydrocarbons as hereinunder defined,

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have near-azeotropic behaviour, are non-flammable up to an hydrocarbon content of about 4% by weight or only slightly flammable for an hydrocabon content higher than 4% and up to 10% by weight and are characterized by vapour pressure curves such as to make them particularly suitable as substituents for refrigerants R-12, by enjoying moreover of the feature of being "drop-in". Such mixtures are moreover characterized by a very low or zero environmental impact, expressed in terms of ODP, GWP and VOC.

Therefore, object of the present invention are ternary mixtures, utilizable as refrigerating fluids, essentially of the following types:

A)	1,1,1,2-tetrafluoroethane (R134a)	65-94% by weight
	pentafluoroethane (R125)	2-25% by weight
	n-butane (R600)	1-10% by weight
B)	1,1,1,2-tetrafluoroethane (R134a)	65-94% by weight
	pentafluoroethane (R125)	2-25% by weight
	isobutane (R600a)	1-10% by weight
C)	1,1,1,2-tetrafluoroethane (R134a)	65-94% by weight
	pentafluoroethane (R125)	2-25% by weight
	n-butane (R600) and isobutane (R600a)	1-10% by weight
D)	1,1,1,2-tetrafluoroethane (R134a)	65-94% by weight
	1,1,1,2,3,3,3-heptafluoropropane (R227ea)	5-25% by weight
	n-butane (R600)	1-10% by weight
E)	1,1,1,2-tetrafluoroethane (R134a)	65-94% by weight
	1,1,1,2,3,3,3-heptafluoropropane (R227ea)	5-25% by weight
	isobutane (R600a)	1-10% by weight
F)	1,1,1,2-tetrafluoroethane (R134a)	65-94% by weight
	1,1,1,2,3,3,3-heptafluoropropane (R227ea)	5-25% by weight
	n-butane (R600) and isobutane (R600a)	1-10% by weight,

said mixtures having the feature that the percent variation of the vapour pressure after the 50% evaporation of the liquid at the temperature of 25°C is comprised between 0.5 and 15% of the vapour pressure before said evaporation and preferably between 0.5 and 7%. The n-butane is usually a commercial product which can contain up to 10% of isobutane. Similarly, isobutane is usually a commercial product which can contain up to 10% of n-butane.

Preferably A, B and C mixtures contain 75-86% of R134a, 4-20% of R-125 and 2-4% of hydrocarbon (R-600 and/or R-600a); the D, E and F mixtures contain 75-93% of R-134a, 5-20% of R-227ea and 2-4% of hydrocarbon (R-600 and/or R-600a), since these mixtures result non flammable. Unexpectedly, as already said, the mixtures containing only a little more than 4% of hydrocarbon result slightly flammable. Moreover the mixtures containing n-butane are preferred to those containing isobutane; this was unexpected as the azeotropic or near-azeotropic behaviour usually is found more easily when the boiling points of the components are closer.

Generally, the mixtures object of the present invention, being constituted by more refrigerants, show the advantage of a greater flexibility and therefore they meet better than one single component the thermodynamic and thermophysical characteristics required for a certain refrigerating circuit configuration.

As already said, the above mentioned mixtures are substituents of R-12 of drop-in type, as they can be used in the existing equipments concerning refrigeration at middle evaporation temperature, in particular in the domestic refrigeration, without needing the replacement of mechanical parts or of conventional mineral lubricating oils. This feature was unexpected if it is considered that the drop-in substituents of R-12 previously known contain chlorine. Once dissolved in the lubricating oil the invention mixtures, unlike those previously used, do not cause, also at high temperatures and for long contact times, noticeable alterations in the chemical-physical characteristics of both the oil and the metal surfaces usually present in the refrigerating circuits, revealing therefore a good chemical stability.

Moreover, thanks to the near-azeotropic characteristics, depending on the content of hydrocarbons, said mixtures show no or at most a slight tendency to fractionate into inflammable liquids or vapours also after a substantial evaporation of around 50% by weight.

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It has also been unexpectedly found that even small percent amounts of n-butane or isobutane present in these mixtures allow to noticeably improve the solubility of conventional mineral lubricants in HFC, notoriously incompatible with these oils. Moreover is has been noticed that also when the solubility of the oil in the refrigerant is not optimum, the lubricating oil is unexpectedly capable of coming back from the evaporator, which represents the critical zone of the cir-
5 cuit, to the compressor, thus maintaining lubrication and avoiding wear phenomena of the compressor mechanical parts and undesired oil accumulations in the exchangers.

Some working examples of the present invention are hereinunder reported, whose purpose is merely illustrative but not limitative of the scope of the invention.

10 **EXAMPLES 1-9 and 15, COMPARATIVE EXAMPLES 10-14 and 16-17**

Various mixtures according to the present invention were prepared: the compositions, expressed as % by weight, are reported in Table 1. Each mixture was characterized according to the following tests:

15 **(a) Near-azeotropic behaviour**

The mixture, of known composition and weight, was introduced into a previously evacuated small cylinder having an internal volume equal to 150 cm^3. The filling volume ratio was initially equal to 0.8. The cylinder was introduced into a thermostatic bath at 25°C. As soon as the equilibrium was reached, the inner pressure was measured by means of a pressure transducer. The content of the cylinder was then partly discharged by means of a suitable
20 valve, until the cylinder weight reached a value corresponding to 50% of the initial charge, by keeping the temperature at 25°C. The pressure inside the tube was measured again at 25°C. The mixture had a near-azeotropic behaviour if the pressure drop, expressed as percentage with respect to the initial pressure ($\Delta p/p \cdot 100$), was comprised between 0.5 and 15%, preferably between 0.5 and 7%. For some mixtures also the value corresponding to the 90% evaporation of the starting mixture was reported.

25 Although the $\Delta p/p \cdot 100$ value is not the direct measurement of the azeotropy, it is however indicative of an azeotropic behaviour.

In order to more stress the behaviour closer to the azeotropic one of the mixtures according to the invention compared with the mixtures of the prior art, there was measured the variation of the composition versus the amount of evaporated liquid at the temperature of 25°C for a typical mixture according to the invention and for two mixtures of
30 similar composition of the type described in **EP 565265**. The results are reported in Table 2. The composition of the comparative examples 14 of Table 1 and 17 of Table 2 practically reproduces the composition of example 2 of EP 565265. The improvement represented by the compositions of the invention results evident.

(b) Boiling temperature

By using the same cylinder described above, filled with the refrigerating mixture up to a volume ratio of 0.8 and
35 immersed into the thermostatic bath, the boiling temperature is determined by slowly reducing the temperature of the thermostatic bath until the equilibrium pressure of 1.013 bar is reached: the temperature corresponding to such a pressure is the boiling temperature of the mixture.

(c) Inflammability

The inflammability of the tested mixtures was determined according to a test which allowed to reveal flame propa-
40 gation when the test mixture was supplied onto a burner put at a determined distance.

A burner with oxidizing flame constituted by a Bunsen burner was put near the zero point of a graduated horizontal rod, so that the third upper part of a 5 cm flame was at the same height of the delivering valve of a small spray cylinder. The test mixture was introduced in the cylinder and thermostated at the temperature of 20°C. The cylinder was put at the distance of 15 cm from the burner and the liquid phase of the mixture was supplied onto the flame.

45 The following inflammability evaluation criteria were adopted: the mixture was considered non-flammable if no propagation or increase of the burner flame was noticed; the mixture was considered slightly flammable if a slight increase of the flame without propagation was noticed; the mixture was considered flammable if propagation of the flame was noticed independently of the flame length.

In case of the refrigerating mixtures of the invention the test was carried out on both liquid phases and on vapor
50 phases at the equilibrium. Before carrying out the test all the mixtures were analyzed by gaschromatographic technique; the vapour phase of the mixtures was restored as liquid phase and delivered according to the test modalities. For comparative purposes the data obtained with the binary mixtures R-134a/R-600 and R-134a/R-600a are reported. The presence of R-125 and R-227ea in the compositions according to the invention allows to improve the characteristics of non-flammability compared with said binary mixtures.

55 **(e) ODP and GWP**

They were calculated on the basis of the known values of the pure components constituting the mixture (weighted average), referred to CFCl$_3$.

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EXAMPLE 18

Solubility of mineral oil in refrigerating mixtures.

A reference mineral oil (SHELL/CLAVUS 32) was introduced in a glass test tube having thick walls resistant to high pressures and closed at one end by a metal valve. After cooling, the refrigerating mixture to be tested was introduced in the test tube previously evacuated and the test tube was immersed in a thermostatic bath. The temperature was firstly slowly increased from 25°C up to 60°C (homogenous solution) and then reduced until clouding was noticed (cloudy point).

The experimental values obtained with the mixture R-125/R-134a/R-600 in the 10,90/84, 16/4,94 ratio and for comparative purposes, with R-134a and R-12, are reported in Table 3.

EXAMPLE 19: Wear test

The test allows to point out possible anomalies in the compressor lubrication by observing the mechanical parts wear. The wear phenomena are connected to insufficient lubrication caused by poor return of the oil to the compressor or by noticeable decrease of the viscosity of the oil/refrigerant system which is no longer capable of lubricating the compressor mobile parts.

In a test refrigerant circuit, equipped with an alternative hermetic compressor for home refrigerators, a liquid mixture consisting of R-125/R-134a/R-600 in ratio by weight 10:85:5 is introduced. The used lubricating oil is a mineral oil ISO 32, commonly used with R-12. The compressor is kept in continuous working for 1000 hours, by adjusting the delivery pressure at 20 bar. This period being elapsed the compressor mechanical parts are submitted to a visual observation, in order to identify anomalous wear phenomena. The evaluations are carried out on the basis of a comparative test with the conventional refrigerant R-12. The refrigerant and oil amounts in the two tests are the same. The results are reported in Table 4.

EXAMPLES 20 and 21: Tests of chemical stability

The mixtures according to the invention were submitted to a chemical stability test in the presence of metals (copper and steel), according to ASHRAE Method 97-1983, with some minor modifications, as reported hereinafter.

One copper and one steel coupon and about 1 ml of mineral oil such as SHELL CLAVUS 32 were introduced into a glass tube, having a 4.5 mm diameter and a 250 mm height.

The glass tube was then inserted into a steel cylinder fitted to contain exactly the tube, and equipped with a valve. The cylinder was evacuated, cooled and then loaded with 1 ml of refrigerating mixture. The cylinder was then closed and put in a stove at 175°C for 14 days.

After such treatment, the refrigerant was analyzed by gaschromatography to detect the presence of possible byproducts deriving from degradation reactions of the refrigerant. The oil was titrated to determine the possible increase of the acidity (expressed as mg KOH/g oil). The metal coupons were submitted to visual examination to reveal possible surface changes due to corrosion and formation of deposits.

The evaluations are carried out by considering as reference a system constituted by R-12/oil/metals. The results obtained with the two mixtures according to the invention are reported in Table 5.

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TABLE 1 - Near-azeotropic compositions: chemical-physical data

Ex.	Composition (% by weight)	Vapour tension at 25°C (bar)	Density at 25°C	Vapour composition in equilibrium at 25°C (% by weight)	Near-azeotropic behaviour (ΔP/p 100) -50% -90%	B.P. °C	Flammability ** Liq.Vap.	ODP ***	GWP ***
1	R-125 9.8 R-134a 85.3 R-600 4.9	7.83	1.14	R-125 17.2 R-134a 76.4 R-600 6.4	4.72 10.98	-30.0	S.F. S.F.	0	0.32
2	R-125 10.4 R-134a 85.6 R-600 4.0	7.78	1.15	R-125 16.0 R-134a 78.8 R-600 5.2	5.14 10.92	-29.8	N.F. S.F.	0	0.33
3	R-125 16.6 R-134a 81.0 R-600 2.4	8.15	1.17	R-125 25.9 R-134a 70.8 R-600 3.3	5.77 13.50	-32.0	N.F. N.F.	0	0.36
4	R-125 12.8 R-134a 84.6 R-600 2.6	7.79	1.17	R-125 20.6 R-134a 75.8 R-600 3.6		-31.0	N.F. N.F.	0	0.35
5	R-125 6.6 R-134a 91.0 R-600 2.4		1.17			-29.0	N.F.	0	0.31
6	R-125 10.6 R-134a 86.3 R-600a 3.1		1.16	R-125 16.4 R-134a 78.7 R-600a 4.9		-33.0	N.F. S.F.	0	0.33
7	R-125 9.1 R-134a 85.8 R-600a 5.1	7.95	1.14	R-125 14.3 R-134a 78.2 R-600a 7.5	5.03 12.08	-34.0	S.F. F.	0	0.32
8	R-227ea 24.0 R-134a 71.0 R-600 5.0	6.60	1.18	R-227ea 19.3 R-134a 74.0 R-600 6.7	2.88 5.30	-26.0	N.F. S.F.	0	0.40
9	R-227ea 9.0 R-134a 86.0 R-600a 5.0	7.35	1.15	R-227ea .... R-134a R-600a	4.15 9.98	-32.0		0	0.32
10*	R-12 100	6.43	1.22	R-12 100	0.00 0.00	-29.5	N.F. N.F.	1	2.93
11*	R-134a 94.9 R-600 5.1		1.14	R-134a 93.0 R-600 7.0		-27.0	F. F.	0	0.27
12*	R-134a 95.0 R-600a 5.0		1.14	R-134a 91.5 R-600a 8.5		-32.5	F. F.	0	0.27
13*	R-218 9.2 R-134a 85.8 R-600a 5.0	8.19	1.15	R-218 17.8 R-134a 75.7 R-600a 6.5	7.69 15.26	-36.0		0	
14*	R-218 8.7 R-134a 85.9 R-290 5.4	9.85	1.10	R-218 17.5 R-134a 69.5 R-290 13.0	20.81 31.67	-45.0		0	

* comparative example
** F. = flammable; N.F. = non flammable; S.F. = slightly flammable.
*** with respect to CFCl$_3$

TABLE 2 - Variation of composition versus the amount of liquid evaporated at the temperature of 25°C.

Ex.	Compo-nents	Initial composition and after evaporation of 50 and of 90% by weight (% by weight)						Variation of the liquid composition (Δ% in peso)		% Variation of the components in the liquid (Δ%/C_i %)	
		C_i liq.	vap.	$C_{(-50\%)}$ liq.	vap.	$C_{(-90\%)}$ liq.	vap.	after 50% evap.	after 90% evap.	after 50% evap.	after 90% evap.
15	R-125	9.8	17.2	5.0	11.8	2.5	2.9	-4.8	-7.3	-49.0	-74.5
	R-134a	85.3	76.4	91.5	82.7	95.4	94.8	+6.2	+10.1	+7.3	+11.8
	R-600	4.9	6.4	3.5	5.5	2.1	2.3	-1.4	-2.8	-28.6	-57.1
16*	R-218	9.2	17.8	3.5	9.6	0.4	1.4	-5.7	-8.8	-62.0	-95.6
	R-134a	85.8	75.7	92.9	84.5	98.4	96.2	+7.1	+12.6	+8.3	+14.7
	R-600a	5.0	6.5	3.6	5.9	1.2	2.4	-1.4	-3.8	-28.0	-76.0
17*	R-218	8.7	17.5	3.1	9.0	0.2	0.6	-5.6	-8.5	-64.4	-97.7
	R-134a	85.9	69.5	95.7	86.2	99.7	99.3	+9.8	+13.8	+11.4	+16.1
	R-290	5.4	13.0	1.2	4.8	0.1	0.1	-4.2	-5.3	-77.7	-98.1

* comparative example

TABLE 3

Solubility of mineral oil in refrigerating mixtures			
Concentration of the oil (*) % by weight	Demixing critical temperature (cloudy point) °C		
	Example 18 R-125/R-134a/R-600 = 10,90/84,16/4,94	R-134a	R-12
0.14	+12	+36	< -70
0.20		+45	< -70
0.23	+18	+49	
0.30	+24	+58	< -70
0.35	+30		< -70
1.94		> +60	
2.03	> +60		

* Olio SHELL/CLAVUS 32

TABLE 4

Wear tests of the compressor (*).		
Mechanical parts	Example 19 R-125/R-134a/R-600 = 10/85/5	R-12
SHAFT:		
eccentric	1	1
long shank	2	1
BODY:		
cylinder	1	1
hub	1	1
PISTON	1	1
CONNECTING ROD	1	1
VALVE	SD	SC
PLATE VALVE	SD	SC

(*) Analysis codification:
1 Homogeneous slight polishing without scorings
2 Non homogeneous slight polishing without scorings
SD Slight deposit
SC Slight colouring

TABLE 5

Chemical stability tests (Modified ASHRAE TEST 97-1983 14 days at 175°C) (*)						
	Comparison		Example 20		Example 21	
Refrigerant (% by weight)	R-12	100	R-125	10.0	R-227ea	24.0
			R-134a	85.0	R-134a	71.0
			R-600	5.0	R-600	5.0
Humidity in the refrigerant	13 ppm		15 ppm		15 ppm	
Oil	mineral		mineral		mineral	
Humidity in the oil	35 ppm		35 ppm		35 ppm	
Metal	Cu; AISI-316		Cu; AISI-316		Cu; AISI-316	
RESULTS						
Visual evaluation:						
Cu		B		B		B
AISI-316		U		U		U
oil		SC		SC		SC
Acidity (mg KOH / g oil):						
before	< 0.01		< 0.01		< 0.01	
after	0.15		0.08		0.09	
Gaschromatographic analysis:						
by-products (% by weight)	0.18 (**)		< 0.01		< 0.01	

(*) Analysis codification:
SC = slight colouring
U = unaltered
B = browning
(**) by product R-22

Claims

1. Ternary compositions of hydrofluorocarbons with n-butane or isobutane selected from the group consisting of:

A)	1,1,1,2-tetrafluoroethane (R134a)	65-94% by weight
	pentafluoroethane (R125)	2-25% by weight
	n-butane (R600)	1-10% by weight
B)	1,1,1,2-tetrafluoroethane (R134a)	65-94% by weight
	pentafluoroethane (R125)	2-25% by weight
	isobutane (R600a)	1-10% by weight
C)	1,1,1,2-tetrafluoroethane (R134a)	65-94% by weight
	pentafluoroethane (R125)	2-25% by weight
	n-butane (R600) and isobutane (R600a)	1-10% by weight
D)	1,1,1,2-tetrafluoroethane (R134a)	65-94% by weight
	1,1,1,2,3,3,3-heptafluoropropane (R227ea)	5-25% by weight
	n-butane (R600)	1-10% by weight
E)	1,1,1,2-tetrafluoroethane (R134a)	65-94% by weight
	1,1,1,2,3,3,3-heptafluoropropane (R227ea)	5-25% by weight
	isobutane (R600a)	1-10% by weight
F)	1,1,1,2-tetrafluoroethane (R134a)	65-94% by weight
	1,1,1,2,3,3,3-heptafluoropropane (R227ea)	5-25% by weight
	n-butane (R600) and isobutane (R600a)	1-10% by weight,

said compositions having the feature that the percent variation of the vapour pressure after 50% evaporation of liquid at the temperature of 25°C is comprised between 0.5 and 15% of the vapour pressure before said evaporation.

2. Compositions according to claim 1 consiting of:

1,1,1,2-tetrafluoroethane (R134a)	75-86% by weight
pentafluoroethane (R125)	4-20% by weight
n-butane (R600)	2-4 % by weight

3. Compositions according to claim 1 consisting of:

1,1,1,2-tetrafluoroethane (R134a)	75-86% by weight
pentafluoroethane (R125)	4-20% by weight
isobutane (R600a)	2-4 % by weight

4. Compositions according to claim 1 consisting of:

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1,1,1,2-tetrafluoroethane (R134a)	75-86% by weight
pentafluoroethane (R125)	4-20% by weight
n-butane (R600) and isobutane (R600a)	2-4 % by weight

5. Compositions according to claim 1 consisting of:

1,1,1,2-tetrafluoroethane (R134a)	75-93% by weight
1,1,1,2,3,3,3-heptafluoropropane (R227ea)	5-20% by weight
n-butane (R600)	2-4% by weight

6. Compositions according to claim 1 consisting of:

1,1,1,2-tetrafluoroethane (R134a)	75-93% by weight
1,1,1,2,3,3,3-heptafluoropropane (R227ea)	5-20% by weight
isobutane (R600a)	2-4 % by weight

7. Compositions according to claim 1 consisting of:

1,1,1,2-tetrafluoroethane (R134a)	75-93% by weight
1,1,1,2,3,3,3-heptafluoropropane (R227ea)	5-20% by weight
n-butane (R600) and isobutane (R600a)	2-4% by weight.

8. Compositions according to anyone of claims from 1 to 7 wherein the percent variation of the vapour pressure after 50% evaporation of the liquid at the temperature of 25°C is comprised between 0.5 and 7% of the vapour pressure before said evaporation.

9. Use of the compositions according to claims from 1 to 8 as refrigerating fluids.

10. Use of the compositions according to claims from 1 to 8 as "drop-in" substituents for R-12 refrigerant.

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European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 96 11 9764

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Y	WO 92 17558 A (DU PONT DE NEMOURS) * abstract; claims 1,6,7,13,29 * ---	1-10	C09K5/04 C09K3/30
Y	WO 94 00529 A (GREAT LAKES CHEMICAL CORPORATION) * abstract; claims 1,10,14 * ---	1-10	
A,D	US 4 174 295 A (BARGIGIA) * abstract; claims 1,4 * ---	1-10	
A,D	EP 0 384 371 A (HOECHST) * abstract; claims 1,5 * -----	1-10	

TECHNICAL FIELDS
SEARCHED   (Int.Cl.6)

C09K

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	17 February 1997	Nicolas, H

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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